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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08K 5/09	A2	(11) International Publication Number: **WO 99/48963** (43) International Publication Date: 30 September 1999 (30.09.99)

(21) International Application Number: PCT/US99/06379

(22) International Filing Date: 24 March 1999 (24.03.99)

(30) Priority Data:

330077	25 March 1998 (25.03.98)	NZ
09/127,316	31 July 1998 (31.07.98)	US

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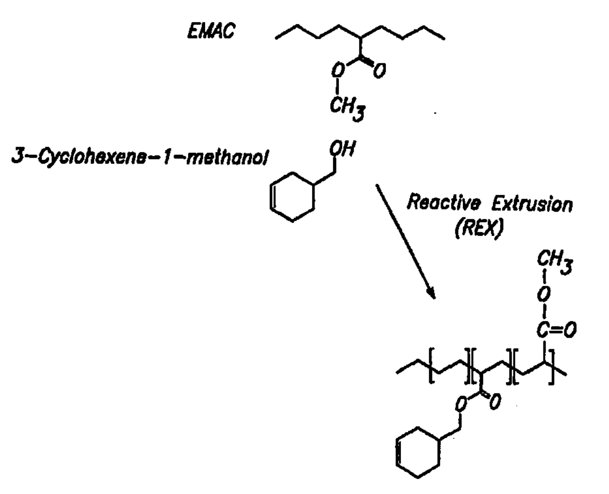
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

Without international search report and to be republished upon receipt of that report.

(54) Title: OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS



EMCM
poly(ethylene/methyl acrylate/cyclohexene-methyl acrylate)

(57) Abstract

An oxygen scavenger composition, for use in or with plastics materials, includes a polymer or oligomer having at least one cyclohexene group or functionality. The composition produces only low levels of volatile or (extractable from a plastics material in which it is incorporated) products as a consequence of oxygen scavenging. A family of polymers containing selected cyclic allylic pendent groups for oxygen scavenging packaging which has minimal organoleptic by-products after oxidation. Multilayer plastic containers for food and beverage packaging which incorporate oxygen scavenging resins which selectively oxidize upon activation without giving off odorous fragments.

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OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS

Field of the Invention

The present invention is directed to oxygen scavengers for use in plastics materials, and in particular plastics films. Emphasis is given to scavengers which produce low or negligible levels of oxidation by-products which may contaminate the head space in a package. This invention also relates to a composition useful in scavenging oxygen from environments containing oxygen-sensitive products, particularly food and beverage products. More specifically, the oxygen scavenging composition includes a polymer having ethylenic unsaturation contained within a cyclic moiety, a transition metal compound and, optionally, a photoinitiator. The present invention also relates to compositions for use in areas such as food packaging, and with minimal effect on odor and taste of packaged contents. The invention preferably uses ethylene acrylate copolymers which are modified with selected cyclic allylic pendent groups for use in oxygen scavenging packaging materials. The present invention also relates to rigid polymeric food or beverage containers comprising polyester such as polyester terephthalate or polyester naphthalate and oxygen scavenging polymer.

Background of the Invention

The majority of plastic films produced are employed in some form of packaging. The present invention is primarily concerned with those films used for applications requiring a low level of oxygen in a package, though may also find other uses.

Limiting the exposure of oxygen-sensitive products to oxygen maintains and enhances the quality and shelf life of many products. For instance, by limiting the oxygen exposure of oxygen-sensitive food products in a packaging system, the quality of the food product can be maintained and spoilage retarded. In addition, such packaging also keeps the product in inventory longer, thereby reducing costs incurred from waste and having to restock.

In the food packaging industry, several techniques for limiting oxygen exposure have been developed. Common techniques include those where oxygen is consumed within the packaging environment by some means other than the packaged article or the packaging material (e.g., through the use of oxygen scavenging sachets), those where reduced oxygen environments are created in the package (e.g., modified atmosphere packaging (MAP) and vacuum packaging), and those where oxygen is prevented from entering the packaging environment (e.g., barrier films).

The art dealing with barrier packaging, and the low oxygen or modified packaging of products is relatively well developed. This includes the use of films and inserts containing oxygen scavenging compounds able to extract a majority of any residual oxygen after packaging occurs.

Oxygen scavenging compounds for use in plastic films are relatively well known. Typically these comprise unsaturated compounds in combination with a transition metal catalyst. In response to some form of initiation—usually exposure to light or radiation—the scavengers react with available oxygen in the package.

For instance:

Michael Rooney, "Oxygen scavenging: a novel use of rubber photo-oxidation", *Chemistry and Industry*, March 20, 1982, pp. 197-198, describes the use of ethylenically unsaturated compounds as oxygen scavengers on exposure to light. However, systems describing the use of transition metal catalysts are not described.

US 4,908,151 to Mitsubishi describes sachets containing unsaturated fatty acid (i.e., an ethylenically unsaturated hydrocarbon) in combination with a transition metal compound in a basic substance. However, there is no description of these materials in the form of a film nor the use of photo-exposure as an initiating mechanism.

Japanese patent JP5032277 to Kuwa describes the use of radical containing resin layers in packages. The invention comprises an oxidizable polymer whose oxygen scavenging abilities is photoinitiated.

New Zealand patent application NZ241802 to W R Grace and also NZ243077 also to W R Grace, claim oxygen scavenging compositions comprising ethylenically unsaturated hydrocarbons with transition metal catalysts. A wide range of ethylenically unsaturated compounds are discussed in the texts of these specifications though there is no mention of the problems to which the present invention is directed, nor the compounds and products encompassed by the present invention.

Sachets containing an oxygen scavenging compositions can contain ferrous compositions, which oxidize to their ferric state, unsaturated fatty acid salts on an absorbent, and/or a metal-polyamide complex. See, e.g., U.S. Patent Nos. 4,908,151 and 5,194,478. The disadvantages of sachets include the need for additional packaging steps (to add the sachet to the package), the

potential for contamination of the packaged article should the sachet break and the danger of ingestion by a consumer.

Oxygen scavenging materials also have been incorporated directly into the packaging structure. This technique (hereinafter referred to as "active oxygen barrier") can provide a uniform scavenging effect throughout the package and can provide a means of intercepting and scavenging oxygen as it passes through the walls of a package, thereby maintaining the lowest possible oxygen level throughout the package. Active oxygen barriers have been formed by incorporating inorganic powders and/or salts as part of the package. See, e.g., U.S. Patent Nos. 5,153,038, 5,116,660, 5,143,769, and 5,089,323. However, incorporation of such powders and/or salts can degrade the transparency and mechanical properties (e.g., tear strength) of the packaging material and can complicate processing, especially where thin films are desired. Also, these compounds as well as their oxidation products can be absorbed by food in the container, which can result in the food product failing to meet governmental standards for human consumption.

EP 0 519 616 discloses an oxygen scavenging composition that includes a blend of an epoxide, a first polymeric component grafted with an unsaturated carboxylic anhydride and/or acid, a second polymeric component including OH, SH, or NHR^2 groups where R^2 is H, C_1-C_3 alkyl, or substituted C_1-C_3 alkyl moiety, and a metal salt capable of catalyzing the reaction between oxygen and the second polymeric component. The first polymeric component is present in an amount sufficient to ensure that the blend is non-phase separated. A blend of polymers is utilized to obtain oxygen scavenging, and the second polymeric component is preferably a (co)polyamide such as MXD6.

Another type of active oxygen barrier is illustrated in EP-A-0 301 719, EP-A-0 380 319, PCT Publication No. WO 90/00578, and PCT Publication No. WO 90/00504. See also U.S. Patent Nos. 5,021,515 5,194,478, and 5,159,005. The disclosed oxygen scavenger includes polyamide-transition metal catalyst compositions. Through catalyzed scavenging by the polyamide, the package wall regulates the amount of oxygen reaching the interior of the package. However, the onset of useful oxygen scavenging (i.e., up to about 5.8×10^{-5} $cm^3/m^2 \bullet 24$ hours at ambient conditions) can take as long as 30 days to occur. Therefore, this technique is not acceptable for many applications. Further, polyamides typically are incompatible with many thermoplastic polymers commonly used to make flexible packaging materials (e.g., ethylene/vinyl acetate copolymers, low density polyethylene, etc.) or, when used by themselves, are difficult to process and result in inappropriately stiff structures.

Oxygen scavenging compositions that include transition metal catalysts and ethylenically unsaturated hydrocarbon polymers which have an ethylenic double bond content of from 0.01 to 10 equivalents per 100 grams of polymer are disclosed in U.S. Patent No. 5,399,289. Various conventional homopolymers, copolymers, and polymer blends are disclosed. Because these polymers are amorphous, they can be difficult to blend and process with film-forming semicrystalline polymers conventionally used to make flexible packaging materials.

The use of a transition metal and a photoinitiator to facilitate initiation of effective scavenging activity of ethylenically unsaturated compounds is taught in U.S. Patent No. 5,211, 875, which is incorporated herein by reference as if set forth in full.

PCT Publication Nos. WO 95/02616 and WO 96/40799 disclose a scavenger composition that includes a transition metal salt and a copolymer (of ethylene and a vinyl monomer) having ether, amino, carboxylic acid, ester, or amide functionalities pendent therefrom. Although these compositions can provide oxygen scavenging activity, the particular advantages of having ethylenic unsaturation contained within a cyclic moiety are not disclosed. Because the compositions of this invention are significantly cleaner than those described in the prior art, they do not require the use of high levels of adjuncts to absorb the undesirable byproducts. Such absorbent additives are known in the art, for example see U.S. 5,834,079 and U.S. 08/857,276. It is also well known in the art that such additives (zeolites and silicas) adversely affect the haze and clarity of packaging structures.

PCT Application WO 96/40799 from Chevron describes the use of a variety of ethylenic materials with benzylic, allylic or ether containing side chains. Some of these materials may be prepared by esterification or transesterification of a polymer melt. The use of pendent cyclic groups containing allylic unsaturation is generally referred to, but there is only one such example, wherein Nopol, a bicyclic alcohol, is used in a transesterification reaction and oxygen absorbing films are formulated from the product. There is no reference to the benefits of cyclic allylic compounds as described in this invention i.e., on oxidation they produce very low levels of oxidation byproducts when compared to comparable linear allylic systems. Because of its bicyclic nature, Nopol is not expected to produce these benefits.

While the prior art compounds may effectively scavenge oxygen they introduce other problems into packaging. For instance, in summary the prior art incorporates into film structures compounds which are ethylenically unsaturated but which often cleave as a consequence of the reactions of the oxygen scavenging process. For example, films containing unsaturated

compounds such as squalene or vegetable oils produce large amounts of volatile aldehydes and ketones upon oxidation. Unfortunately, many of these volatile compounds are not contained within the film structure and find their way into the head space of the package. Here they can represent more of a problem than the oxygen which they have replaced and have the potential to contaminate comestible products.

This problem represents a significant problem yet has been downplayed or overlooked by the published prior art. As a consequence, those searching the prior art for a solution to this problem find no answer—the art appears to be directed primarily along a narrow track of improving on scavenging efficiencies, or physical properties of scavenging films, rather than recognizing or addressing other associated problems.

Accordingly the present invention seeks to address the problems associated with scission products of oxygen scavengers, and seeks also to provide a group of compounds and substances (as well as films and plastics materials including same) which have an advantage over the prior art in terms of reduced quantities of scission products.

Ideally, a polymeric material for use in an oxygen scavenging composition should exhibit good processing characteristics, be able to be formed into useful packaging materials or have high compatibility with those polymers commonly used to make packaging materials, and not produce byproducts which detract from the color, taste, or odor of the packaged product. It has been found that when the ethylenic unsaturation is contained within a cyclic group, substantially fewer and less byproducts are produced upon oxidation as compared to analogous non-cyclic materials. Optimally, a packaging

material formed from such a composition can retain its physical properties after significant oxygen scavenging.

New polymer compositions having properties that are particularly tailored for specific applications are required in response to more specific and sophisticated end uses. It can be difficult to make these compositions directly by polymerization from monomers or via solution esterification or transesterification, but manufacturing them in melt mixing equipment such as an extruder has provided an efficient, economical and viable means to supply increasingly complex polymers to meet the needs in specialized markets.

It is well known that regulating the exposure of oxygen-sensitive products to oxygen maintains and enhances the quality and "shelf-life" of the product. For instance, by limiting the exposure of oxygen sensitive food products to oxygen in a packaging system, the quality or freshness of food is maintained, spoilage reduced and the food shelf life extended. In the food packaging industry, several means for regulating oxygen exposure have already been developed. These means include modified atmosphere packaging (MAP) and oxygen barrier film packaging.

One method currently being used is "active packaging", whereby the package containing the food product has been modified in some manner to regulate the food's exposure to oxygen. One form of active packaging uses oxygen-scavenging sachets which contain a composition which scavenges the oxygen through oxidation reactions. One type of sachet contains iron-based compositions which oxidize to their ferric states. Another type of sachet contains unsaturated fatty acid salts on a particulate adsorbent. Yet another sachet contains metal/polyamide complex. However, one disadvantage of

sachets is the need for additional packaging operations to add the sachet to each package. A further disadvantage arising from the iron-based sachets is that certain atmospheric conditions (e.g., high humidity, low CO_2 level) in the package are sometimes required in order for scavenging to occur at an adequate rate. Further, the sachets can present a problem to consumers if accidentally ingested.

Another means for regulating exposure of a packaged product to oxygen involves incorporating an oxygen scavenger into the packaging structure itself. A more uniform scavenging effect through the package is achieved by incorporating the scavenging material in the package instead of adding a separate scavenger structure (e.g., a sachet) to the package. This may be especially important where there is restricted airflow inside the package. In addition, incorporating the oxygen scavenger into the package structure provides a means of intercepting and scavenging oxygen as it permeates the walls of the package (herein referred to as an "active oxygen barrier"), thereby maintaining the lowest possible oxygen level in the package.

One attempt to prepare an oxygen-scavenging wall involves the incorporation of inorganic powders and/or salts. However, incorporation of these powders and/or salts causes reduction of the wall's optical transparency, discoloration after oxidation, and reduced mechanical properties such as tear strength. In addition, these compounds can lead to processing difficulties, especially when fabricating thin films. The oxidation products may migrate into food at levels which would not be regarded as safe or can impart unacceptable taste or smell to food.

An oxygen-scavenging composition comprising a blend of a first polymeric component comprising a polyolefin is known, the first polymeric component having been grafted with an unsaturated carboxylic anhydride or an unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a

second polymeric component having -OH, -SH, or -NHR^2 groups where R^2 is H, C_1-C_3 alkyl, substituted C_1-C_3 alkyl; and a catalytical amount of metal salt capable of catalyzing the reaction between oxygen and the second polymeric component, the polyolefin being present in an amount sufficient so that the blend is not phase-separated. A blend of polymers is utilized to obtain oxygen scavenging, and the second polymeric component is preferably a polyamide or a copolyamide such as the copolymer of m-xylylene-diamine and adipic acid (MXD6).

Some oxygen scavenging systems produce an oxygen-scavenging wall. This is done by incorporating a metal catalyst-polyamide oxygen scavenging system into the package wall. Through catalyzed oxidation of the polyamide, the package wall regulates the amount of oxygen which reaches the interior volume of the package (active oxygen barrier) and has been reported to have oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc) oxygen per square meter per day at ambient conditions. However, this system suffers from significant disadvantages.

One particularly limiting disadvantage of polyamide/catalyst materials can be a low oxygen scavenging rate. Adding these materials to a high-barrier package containing air can produce a package which is not generally suitable for creating an internal oxygen level of less than 0.1% within seven days at storage temperatures, as is typically required for headspace oxygen scavenging applications.

There are also disadvantages to having the oxygen-scavenging groups in the backbone or network structure in this type of polyamide polymer. The basic polymer structure can be degraded and weakened upon reaction with oxygen. This can adversely affect physical properties such as tensile or impact strength of the polymer. The degradation of the backbone or network of the

polymer can further increase the permeability of the polymer to those materials sought to be excluded, such as oxygen.

Moreover, polyamides previously used in oxygen scavenging materials, such as MXD6, are typically incompatible with thermoplastic polymers used in most flexible packaging walls, such as ethylene-vinyl acetate copolymers and low density polyethylene. Even further, when such polyamides are used by themselves to make a flexible package wall, they may result in inappropriately stiff structures. They also incur processing difficulties and higher costs when compared with the costs of thermoplastic polymers typically used to make flexible packaging. Even further, they are difficult to heat seal. Thus, all of these are factors to consider when selecting materials for packages, especially multi-layer flexible packages and when selecting systems for reducing oxygen exposure of packaged products.

Another approach to scavenging oxygen is an oxygen-scavenging composition comprising an ethylenically unsaturated hydrocarbon and a transition metal catalyst. Ethylenically unsaturated compounds such as squalene, dehydrated castor oil, and 1,2-polybutadiene are useful oxygen scavenging compositions, and ethylenically saturated compounds such as polyethylene and ethylene copolymers are used as diluents. Compositions utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically have an oily texture as the compound migrates toward the surface of the material. Further, polymer chains which are ethylenically unsaturated in the backbone would be expected to degrade upon scavenging oxygen, weakening the polymer due to polymer backbone breakage, and generating a variety of off-odor/off-taste by-products.

Other oxidizable polymers recognized in the art include "highly active" oxidizable polymers such as poly(ethylene-methyl acrylate-benzyl acrylate), EMBZ, and poly(ethylene-methyl acrylate-tetrahydrofurfuryl acrylate), EMTF,

as well as poly(ethylene-methyl acrylate-nopol acrylate), EMNP. Although effective as oxygen scavengers, these polymers have the drawback of giving off large amounts of volatile by-products and/or strong odors after oxygen scavenging.

Also known are oxygen-scavenging compositions which comprise a transition-metal salt and a compound having an ethylenic backbone and having allylic pendent or terminal moieties which contain a carbon atom that can form a free radical that is resonance-stabilized by an adjacent group. Such a polymer needs to contain a sufficient amount and type of transition metal salt to promote oxygen scavenging by the polymer when the polymer is exposed to an oxygen-containing fluid such as air. Although effective as oxygen scavengers, upon oxidation, we have found that allylic pendent groups on an ethylenic backbone tend to generate considerable amounts of organic fragments. We believe this is a result of oxidative cleavage. We believe these fragments can interfere with the use of allylic pendent groups as oxygen scavengers in food packaging.

Multilayer rigid container structures, which utilize an oxygen scavenging composition, are known. In the container wall, base polymers such as polyethylene terephthalate have been used along with an oxygen scavenger. The resulting multilayer package wall includes at least an oxygen scavenger core layer as well as inner and outer layers having high oxygen barrier qualities. The oxygen scavenger core layer is a combination of at least an oxygen scavenging polymer with post consumer-polyethylene terephthalate (PC-PET). The inner and outer layers include at least oxygen barrier quality PET.

Furthermore, multilayered plastic bottles having oxygen scavenging capacity sufficient to maintain substantially zero or near zero presence of oxygen in

the bottle cavity under specified storage conditions have also been disclosed. The multilayered bottle wall has at least three layers. The inner and outer layers are PET or another bottling polyester, which define the bottle cavity and the outside skin of the bottle respectively. Between the inner and outer layers is an oxygen scavenging copolyester layer.

Condensation copolymers used for making bottles with polyester such as PET or polyethylene naphthalate (PEN) have also been disclosed. The condensation copolymers comprise predominantly polyester segments and an oxygen scavenging amount of polyolefin oligomer segments. The copolymers are preferably formed by transesterification during reactive extrusion and typically comprise about 0.5 to about 12 wt. % of polyolefin oligomer segments. In a preferred embodiment, a bottle is provided having a multilayer wall of at least three layers. The outer and inner layers are of unmodified PET and the oxygen scavenging layer in between the outer and inner layer is made of the condensation copolymers described above having an oxygen scavenging amount of polyolefin oligomers.

A transparent oxygen-scavenging article for packaging oxygen sensitive products is also known, the oxygen-scavenging article having a multilayered wall including at least three layers, an inner and outer layer of biaxially-oriented aromatic polyester polymers such as PET or PEN and an oxygen-scavenging aromatic ester polymer compatible with the polyester polymer. The oxygen-scavenging aromatic ester polymer must include ketone carbonyl groups to provide the oxygen-scavenging functionality and aromatic and ester groups for compatibility with the polyester.

PET containers have been disclosed that have a container wall of stretched plastic material with high oxygen barrier properties and an activating metal incorporated into the plastic material. The plastic material is PET in admixture

with a polyamide and the metal is either added to the mixture or contained in one or both of the polymers.

A container containing at least one layer containing a plastics material and ions of at least one metal has also been disclosed. The plastics material in the layer consists of at least a partially split or degraded polyamide which has increased sensitivity to reaction with oxygen in the presence of metal thus giving the layer improved oxygen barrier properties.

A container has been disclosed with a wall having high oxygen barrier properties comprising a molded polymer composition, the composition comprising a granular mixture of (1) a first polymer providing essential strength for the container wall and (2) an active component comprising a metal compound capable of scavenging oxygen and consisting essentially of a metal ion having complexing properties and a polymer to which said metal ion is combined as a metal complex in the molded polymer composition of said wall to scavenge oxygen. There is also disclosed a method of producing the polymer composition which can be molded into containers, the method being to treat a polymer with a metal compound dissolved or slurried in a volatile solvent composition during refluxing conditions for obtaining the active component having capacity to scavenge oxygen.

An article has been disclosed with oxygen barrier properties comprising at least partly a molded polymer composition formed by melting granules of the composition and molding the melted composition to produce the article. The composition comprises a granular mixture of (1) a first polymer composition providing strength for the article and (2) a second polymer composition compatible with the first polymer composition. The second polymer composition is obtainable by reacting a polyamide or copolyamide with a solution of a transition metal compound in a volatile solvent under refluxing

conditions. The polymer of the first polymer composition can be any polymer and the metal of the metal compound reacted with the polyamide or copolyamide can be any transition metal. The amount of metal in the second polymer composition is at least 500 ppm.

A polymer material having increased sensitivity to reaction with oxygen has also been disclosed, the polymer material comprising a polyamide, which has been reacted with a nucleophilic reagent and possibly an activator. The nucleophilic reagent is selected from the group consisting of compounds containing at least one hydroxyl group, compounds containing at least one alkoxide group, phosphate compounds, pyrophosphate compounds, polyphosphate compounds, salts of organic acids and a copolymer of vinyl alcohol and ethylene. The activator is in the form of a hydrogen donor. A process is also disclosed for producing the polymer material, which has increased sensitivity of reaction with oxygen. In the process, a polyamide reacts with the nucleophilic reagent under such conditions that the polymer material is obtained.

Such polymeric containers of PET, PEN and/or polyamide as described above utilize oxidizable components to react with and decrease the amount of oxygen in contact with oxygen sensitive materials packaged in containers. All of these oxidizable materials have the disadvantage of imparting unpleasant odor and/or taste to the packaged materials because of the byproducts given off during the oxidation of the oxidizable materials. Another problem is the uncontrolled oxidation fragmentation from the polymer backbone which leads to chain secession, thus weakening the physical integrity of the multilayer container structures.

The present invention solves many of the problems of the prior art, especially with an oxygen scavenging packaging material incorporating polymers comprising cyclic allylic (olefinic) pendent groups which produce little or no migration of oxidation by-products adversely affecting odor or taste, thus minimizing organoleptic problems in food packaging. This is because the cyclic allylic structures are less likely to fragment or cleave after oxidation than the conventional open chain allylic (olefinic) groups used in oxygen scavenging packaging material.

Such polymeric containers of PET, PEN and/or polyamide as described above utilize oxidizable components to react with and decrease the amount of oxygen in contact with oxygen sensitive materials packaged in containers. All of these oxidizable materials have the disadvantage of imparting unpleasant odor and/or taste to the packaged materials because of the byproducts given off during the oxidation of the oxidizable materials. Another problem is the uncontrolled oxidation fragmentation from the polymer backbone which leads to chain secession, thus weakening the physical integrity of the multilayer container structures.

In contrast, the present invention achieves a rigid beverage and food container comprising PET and/or PEN, the container incorporating an oxygen scavenging component of cyclic olefin which does not give off odor and or taste as a result of its oxygen scavenging function. The oxidation also does not cause a change in molecular weight. This is because the cyclic olefin oxygen scavenging component does not fragment as it oxidizes, thus avoiding the problem of imparting oxidation byproducts to the packaged material while maintaining the structural integrity.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description, which is given by way of example only.

SUMMARY OF INVENTION

According to one aspect of the present invention, there is provided an oxygen scavenger for use in or with plastics materials, said scavenger comprising or including a polymer or oligomer having at least one cyclohexene group or functionality.

According to another aspect of the present invention, there is provided an oxygen scavenger, substantially as described above, which produces only low levels of volatile or extractable (from a plastics material in which it is incorporated) products as a consequence of oxygen scavenging.

According to another aspect of the present invention there is provided an oxygen scavenger, substantially as described above, which is substantially stable with respect to reaction with oxygen until triggered by an external event.

According to another aspect of the present invention, there is provided an oxygen scavenger, substantially as described above, wherein the external event is irradiation by electromagnetic radiation.

According to a further aspect of the present invention, there is provided an oxygen scavenging composition, including an oxygen scavenger,

substantially as described above, which includes one or more trigger enhancing components making the scavenger susceptible to triggering from an external event.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, wherein a trigger-enhancing component may be benzophenone or substituted derivatives thereof.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, which includes the presence of one or more catalysts for the scavenging process.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, in which a catalyst may be a transition metal salt, compound or complex.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, which is in the form of a plastics resin.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, in which the plastics resin is a resin suitable for use in the manufacture of plastic films.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, in which the plastic resin is a polyester resin.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, when present in a plastics film or layer thereof.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, when used as a polymeric material of a plastics film, a layer thereof, and/or a coating thereof, or in a plastics material.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, when dispersed throughout a plastics film, a layer thereof, and/or a coating thereon, or in a plastics material.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, in which the anhydride comprises 1,2,3,6-tetrahydrophthalic anhydride or tetrahydrophthalic anhydride monomer derivable from butadiene.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from the reaction of a tetrahydrobenzyl alcohol with one or more compounds having one or more of the following functionalities: carboxylic acid, acid halide, ester, anhydride, and isocyanate.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, in which the alcohol comprises tetrahydrobenzyl alcohol.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, in the compounds with which the alcohol is reacted may include a styrene maleic anhydride copolymer, and/or a polyfunctional isocyanate.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, prepared from a cyclohexene dimethanol compound.

According to another aspect of the present invention, there is provided an oxygen scavenging polymer including at least one pendant cyclohexene group prepared by a reactive extrusion process.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging polymer, substantially as described above, in which the reactive extrusion process comprises an esterification or transesterification step. Suitable catalyst include acids, bases and organometallic compounds such as the titanium alkoxides.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging polymer prepared by a route including a cyclohexene anhydride.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging polymer prepared by a route including the reaction of a diene monomer, or hydroxy containing monomer, with a cyclic anhydride.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging polymer, substantially as described above, in which the cyclic anhydride is a maleic anhydride.

According to a further aspect of the present invention, there is provided an oxygen scavenger including a pendant cyclic alkene group prepared via a method including a Diels Alder addition reaction.

According to another aspect of the present invention, there is provided an oxygen scavenger, substantially as described above, in which the preferred dienes for use in the Diels Alder reaction is substituted and/or unsubstituted 1,3 butadiene.

According to another aspect of the present invention, there is provided an oxygen scavenger, substantially as described above, in which the preferred dienophile for use in the Diels Alder reaction include unsaturated acids, anhydrides, and esters.

According to another aspect of the present invention, there is provided an oxygen scavenger, substantially as described above, in which the cyclic alkene is cyclohexene.

In other aspects, the present invention provides an article which include at least one layer formed from a blend that includes the foregoing composition as well as a method of scavenging oxygen in which a packaging article, at least one layer of which is formed from a blend that includes the foregoing composition, is exposed to actinic or e-beam radiation so as to activate the composition.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from a tetrahydrophthalic anhydride and a polymer or lower molecular weight compound containing at least one amine group.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from diglcidyltetrahydrophthalate.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from the reaction of tetrahydrobenzyl alcohol, methyl or dimethyl substituted tetrahydrobenzyl alcohol with one or more compounds having one or more of the following functionalities: carboxylic acid, acid halide, ester, anhydride, epoxide and isocyanate.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, in which a tetrahydrobenzyl alcohol or substituted tetrahydrobenzyl alcohol reacts with one or more of the following materials:

ethylene (meth)acrylic acid and other acid containing polymers and acid containing lower molecular weight materials;

styrene maleic anhydride copolymers; alpha olefin maleic anhydride copolymers such as octadecene maleic anhydride; ethylene and ethylene alpha olefin maleic anhydride terpolymers; ethylene alkyl (meth) acrylate maleic anhydride terpolymers and other like anhydride containing polymers or anhydride containing lower molecular weight materials;

polymeric or lower molecular weight materials containing acid halide functionality such as poly acryloyl chloride;

ethylene alkyl (meth)acrylate copolymers and terpolymers and alternative polymers or lower molecular weight materials containing lower alkyl ester functionality;

epoxy resins;

isocyanate functional material such as prepolymers and oligomers derived from the common diisocyanates such as MDI, TDI and the like.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from a dihydroxy cyclohexene compound. For example, 3 Cyclohexene-1,1-dimethanol or its substituted derivatives may be used to prepare polyurethane and polyester resins.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen absorbing composition prepared from a cyclohexene carboxylic acid. Such materials may be prepared from acrylic acid and substituted and unsubstituted butadienes. A typical example would be tetrahydrobenzoic acid, derived from acrylic acid and butadiene. This may be reacted with the following materials:

hydroxyl functional materials such as poly(vinyl alcohol) and polyethylene-vinyl alcohol, hydroxyl functional oligomers such as poly(ethylene glycol), the polyester polyols and other lower molecular weight hydroxyl functional materials;

amine functional polymers and lower molecular weight compounds;

polyvalent metal ions.

According to a further aspect of the present invention, there is provided an oxygen scavenger prepared from a cyclohexene functional acid chloride. Example 9 utilizes 3-cyclohexene-1-carbonyl chloride.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from tetrahydrobenzaldehyde and its substituted derivatives. These may be prepared from reaction of butadiene or the methyl substituted butadienes with acrolein.

The tetrahydrobenzaldehydes may be reacted with hydroxyl functional polymers such as poly(vinyl alcohol) and polyethylene-vinyl alcohol to form polyvinyl acetals.

The following definitions apply herein throughout unless a contrary intention is expressly indicated:

"polymer" means the polymerization product of one or more monomers and includes homopolymers, as well as copolymers;
"copolymer" means the polymerization product of two or more kinds of monomers;

"(meth)acrylate" means acrylate or methacrylate;

"photoinitiator" means a substance which, when activated by actinic radiation, enhances and/or facilitates the initiation of one or more properties (e.g.,

oxygen scavenging) in another compound, thus resulting in a shorter induction period and/or an increase in the rate of oxygen uptake of the overall system;

"induction period" means the length of time beginning with the initiation of the active components of a composition and ending with the onset of one or more useful properties (e.g., oxygen scavenging); and

"antioxidant" means a material which can inhibit oxidative degradation and/or crosslinking of a poly polymer so as to, for example, prolong the useful lifetime of the polymer, to stabilize a polymer-containing composition during processing (e.g., extrusion, coating, lamination, etc.); and/or to prolong the shelf-life of the composition (prior to exposure thereof to actinic or e-beam radiation).

The present invention is directed to oxygen scavengers. The invention includes oxygen scavenging substances, as well as compositions containing same. The form of the oxygen scavengers may vary and may comprise small molecules through to large macromolecules as well as those sized in between. The oxygen scavengers will be characterized in that they will be able to react with oxygen in their near vicinity, enabling the removal of oxygen from a closed system.

While the actual form of the oxygen scavengers may vary, a characteristic that they each share is they include cyclic alkene groups or functionalities, which are able to react with oxygen to provide the desired oxygen scavenging properties. In preferred embodiments of the present invention, this will comprise a cyclohexene group i.e. a six-membered ring with double bond between two adjacent carbon atoms. It is acceptable that some carbons of

the cyclohexene group may also form a part of other ring structures within the molecule, and/or form part of the skeleton of the molecule. It is not necessary that the entire C_6 ring be dangling free of the remainder of the molecule to which it is attached. A consideration however is that the group should be so positioned and incorporated into the structure that the double bond is available for reaction with oxygen.

It has been mentioned above that various scavengers of the present invention may take different forms. This will also have some bearing on how they are used, and also produced. Perhaps the simplest embodiments of the present invention are short molecules containing a reactive cyclohexene group, which may be dispersed in an appropriate medium for use. This may include the use of short molecules (see also later) which can be dispersed within a plastics resin or material. The ultimate result would be a plastics film or material incorporating the oxygen scavenger. Of course, consideration would need to be given to accessibility of the scavengers of the oxygen being scavenged though this may rely on the porosity of the film (or film layer/material) in which it is incorporated, or alternatively may be presented in the manner of a coating with a reactive surface.

While the use of oxygen scavengers of varying sizes, (though typically those of smaller size), dispersed through plastics materials is envisaged, oxygen scavengers according to the present invention may also be used in other ways.

For instance, they may be dispersed throughout non-plastics materials. This may include inert and inorganic materials. This may also include other liquids. It is envisaged that such embodiments of the present invention may be used in applications such as sachets inserted into closed packages. The

use of oxygen scavengers in sachets and package inserts is documented in the art and the same principles may be applied here.

Another means by which the present invention may be applied is through the use of plastics resins incorporating the desired scavenging functionalities. These resins, which for instance may include polyester resins, may be used in the various manners by which resins are normally used. This may include film production, resin coatings, as well as molding or extrusion techniques.

Another method by which the present invention may be implemented is the formation or modification of polymers to contain the desired scavenging functionalities and groups. In such cases, the film or plastics material itself will possess oxygen scavenging properties. It is envisaged that such materials may exist as layers in multi-layer films. Such polymers may also be introduced as copolymers or blends in film and plastics manufacturing methods.

The above instances of how embodiments of the present invention may be used are illustrative only. It is noted that the use of oxygen scavenging materials is known in the art, and that art may be drawn upon to further expand the illustrative examples given within this specification.

Embodiments of the present invention based on cyclohexene groups appear to afford significant advantage over the prior art. This advantage is in the number and nature of the oxidation product once the scavenging is completed. In the prior art, heavily reliance is made on straight chain alkenes, such as for instance fatty acids. The problem however, is that film containing unsaturated compounds such as squalene or vegetable oils produce large amounts of volatile aldehydes and ketones upon oxidation. These tend to be released, or leach, from the plastics material over time,

usually find their way into the head space of the packaged material. The presence of these foreign substances can represent a significant problem, which the use of cyclohexene scavenging groups addresses at least partially.

In comparison, there are significantly less scission products from oxidation reactions involving cyclohexene groups—the oxidation of the cyclohexene group does not normally involve ring breakage. If the remainder of the molecule to which the cyclohexene group is attached is bound or linked to the polymeric structure of the material in which it is incorporated or affixed, or otherwise bound or held in place to the material through which it is dispersed or incorporated, then there is little chance of there being any free scission products able to find their way from the film or material structure.

Other aspects of the present invention to some extent parallel the prior art. For instance, it is desirable that the oxygen scavenging materials are relatively stable (with respect to scavenging) until required. In many cases, catalysis and/or triggering of any reaction is required. Photo-initiators such as benzophenone may be included. Initiating or triggering by electromagnetic irradiation (often in the visible through UV regions) is convenient form of triggering and already used in some types of film manufacture. It is also used for triggering many prior art oxygen scavengers and thus employing these features and techniques of the prior art with the present invention is envisaged.

As for most other oxygen scavengers relying on alkenes, some form of catalyst is also required for the oxygen scavenging reactions to proceed effectively. Typically transition metal catalysts are used, including their salts, complexes, and other compounds. These are well documented in the prior art and may also be used with the present invention as appropriate.

According to another aspect of the present invention, there is provided an oxygen scavenging polymer, substantially as described above, in which the reactive extrusion process comprises a transesterification process.

According to one aspect of the present invention, there is provided an oxygen scavenging composition for use in or with plastics materials, said scavenger comprising or including at least one cyclohexene functionality as described above.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, as described above, which produces only low levels of volatile or extractable (from a plastics material in which it is incorporated) products as a consequence of oxygen scavenging.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described herein which is substantially stable with respect to reaction with oxygen until triggered by an external event.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, wherein the external event is irradiation by actinic radiation or electron beam radiation.

According to a further aspect of the present invention, there is provided an oxygen scavenging composition including an oxygen scavenger, substantially

as described above, which includes one or more trigger enhancing components making the scavenger susceptible to triggering from an external event.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, wherein a trigger enhancing component is a photo initiator such as benzophenone or substituted derivatives thereof.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, which includes the presence of pone or more catalysts for the scavenging process.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, in which the catalyst is a transition metal salt, compound or complex.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, which is in the form of a plastic resin.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, in which the plastic resin is a suitable for use in the manufacture of plastics films.

According to another aspect of the present invention, there is provided an oxygen scavenging composition, substantially as described above, in which the plastic resin is a polyester resin.

According to another aspect of the present invention, there is provided an oxygen scavenging article comprising the oxygen scavenging composition described above, where the scavenging component is present as a plastic film or layer thereof.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, when used as a polymeric material of a plastic film a layer thereof, and/or a coating thereof, or in a plastic material.

According to another aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition, substantially as described above, when dispersed through a plastics film, a layer thereof, and/or a coating thereon, or in a plastics material.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from the reaction of a tetrahydrophthalic anhydride or tetrahydrophthalic acid with at least one of a diol, a hydroxy compound or polyhydroxy compound, in the presence of or absence of an esterification catalyst.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition prepared from the reaction of a tetrahydrophthalic anhydride or tetrahydrophthalic acid with at least one of a diol, a hydroxy compound or polyhydroxy compound , in the presence of or absence of an esterification catalyst.

According to a further aspect of the present invention there is provided an oxygen scavenger or oxygen scavenging composition prepared from an ester

or diester of a tetrahydrophthalic anhydride, in the presence of or absence of a transesterification or esterification catalyst.

According to a further aspect of the present invention, there is provided an oxygen scavenger or oxygen scavenging composition substantially as described above, in which the anhydride comprises 1,2,3,6 tetrahydrophthalic anhydride or tetrahydrophthalic anhydride monomers derived from butadiene, 2,3-Dimethyl-1,3-butadiene or isoprene.

According to a further aspect of the present invention, there is provided an oxygen scavenging polymer including at least one cyclohexene group prepared by a reactive extrusion process.

According to the present invention, a composition is provided comprising a polymeric backbone, cyclic olefinic pendent groups and linking groups linking the olefinic pendent groups to the polymeric backbone.
Also according to the present invention, an oxygen scavenging composition is provided comprising a polymeric backbone, cyclic olefinic pendent groups, linking groups linking the olefinic pendent groups to the polymeric backbone and a transition metal catalyst.

Also according to the present invention, an article of manufacture is provided which is suitable as a container, the container inhibiting oxidation of contents of the container by removing oxygen from the container and by inhibiting ingress of oxygen into the container from outside the container, the article comprising an oxygen scavenging composition which comprises a polymeric backbone, cyclic olefinic pendent groups, linking groups linking the olefinic pendent groups to the backbone, and a transition metal catalyst.

Also according to the present invention, a layer suitable for scavenging oxygen is provided which comprises (a) a polymer backbone; (b) cyclic olefinic pendent groups; (c) linking groups linking the backbone with the pendent groups; and (d) a transition metal catalyst.

Also according to the present invention, a process of making a polymer material is provided, the process being selected from the group consisting of esterification, transesterification, amidation, transamidation and direct polymerization, in which the oxygen scavenging packaging material comprises a polymer backbone, cyclic olefinic pendent groups, linking groups linking the backbone with the pendent groups.

In a preferred embodiment of the invention, the polymeric backbone of the above compositions, article, layer and process is ethylenic and the linking groups are selected from the group consisting of:

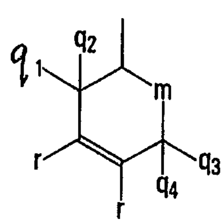
$-O-(CHR)_n-$; $-(C=O)-O-(CHR)_n-$; $-NH-(CHR)_n-$; $-O-(C=O)-(CHR)_n-$;

$-(C=O)-NH-(-CHR)_n-$; and $-(C=O)-O-CHOH-CH_2-O-$;

wherein R is hydrogen or an alkyl group selected from the group consisting of methyl, ethyl, propyl and butyl groups and where n is an integer in the range from 1 to 12.

In a more preferred embodiment of the invention, the cyclic olefinic pendent groups of the above compositions, article, layer and process have the structure (II):

(II)



where q_1, q_2, q_3, q_4, and r are selected from the group consisting of -H, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the range from 0 to 4; and wherein, when r is –H, at least one of q_1, q_2, q_3 and q_4 is –H.

In another preferred embodiment of the invention, the polymeric backbone of the above compositions, article, layer and process comprises monomers selected from the group consisting of ethylene and styrene.
In yet another preferred embodiment of invention, the cyclic olefinic pendent groups of the above compositions, article, layer and process are grafted onto the linking groups of the polymeric backbone by a esterification, transesterification, amidation or transamidation reaction.

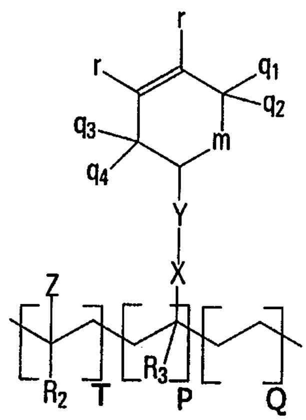
In still another preferred embodiment of the invention, the esterification, transesterification, amidation or transamidation reaction of the above compositions, article, layer and process is a solution reaction or a reactive extrusion.

In another preferred embodiment of the invention, the esterification, transesterification, amidation or transamidation reaction of the above compositions, article, layer and process is catalyzed by a catalyst selected from the group consisting of strong non-oxidizing acids, tertiary amines, Group I alkoxides, Group IVB alkoxides, and Group IVA organometallics.

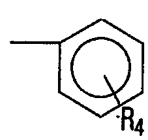
In yet another preferred embodiment of invention, the catalyst of the above compositions, article, layer and process is selected from a group consisting of toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl titanate, tetra-n-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and dibutyltin dilaurate.

In still another preferred embodiment of the invention, the polymeric backbone, linking groups and cyclic olefin pendent groups of the above compositions, article, layer and process comprise repeating units, each unit having a structure (III) as follows:

(III)



wherein P+T+ Q is 100 mol % of the total composition; P is greater than 0 mol % of the total composition; Z is selected from the group consisting of an aryl group; -(C=O)OR$_1$; -O(C=O)R$_1$; and an alkyl aryl group, structure (IV):

(IV) 

where R$_4$ is selected from the group consisting of –CH$_3$, -C$_2$H$_5$, and -H; R$_1$ is selected from the group consisting of -H, -CH$_3$, -C$_2$H$_5$, -C$_3$H$_7$ and -C$_4$H$_9$; R$_2$ and R$_3$ are selected from the group consisting of -H and -CH$_3$; X is selected from the group consisting of -O-, -NH-, -(C=O)O-, -(C=O)NH-, -(C=O)S-, -O(C=O)- and -(CHR)$_\ell$-; ℓ is an integer in the range from 1 to 6; Y is -(CHR)$_n$-, where n is an integer in the range from 0 to 12, R being selected from the group consisting of –H, -CH$_3$ and -C$_2$H$_5$; where q$_1$, q$_2$, q$_3$, q$_4$, and r are selected from the group consisting of -H, -CH$_3$, and -C$_2$H$_5$; and where m is -(CH$_2$)$_n$- and

where n is an integer in the range from 0 to 4; and wherein when r is –H, at least one of q_1, q_2, q_3 and q_4 is –H.

In another preferred embodiment of the invention, the cyclic olefinic pendent groups of the above compositions, article, layer and process are selected from the group consisting of cyclohexene-4-methylene radical, 1-methyl cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical, 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical, 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical, 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical, cyclohexene-4-propylene radical, 1-methyl cyclohexene-4-propylene radical, 2-methyl cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-propylene radical, 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl cyclohexene-4-propylene radical, 2,5-dimethyl cyclohexene-4-propylene radical, 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-methylene radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-methylene radical, 1,2-dimethyl cyclopentene-4-methylene radical, 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical, 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical, 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene

radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and 1,2,3,5-tetramethyl cyclopentene-4-propylene radical.

In yet another preferred embodiment of the invention, the composition of the above compositions, article, layer and process is a ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl acrylate/ethylene copolymer, a cyclohexenyl methyl methacrylate/styrene copolymer, a cyclohexenyl methyl acrylate homopolymer or a methyl acrylate/cyclohexenyl methyl acrylate copolymer.

In another preferred embodiment of the invention, the odor and taste characteristics of products packaged with material comprised of the above compositions, article, layer and process are not adulterated as a result of oxidation of the composition.

In still another preferred embodiment of the invention, there is no significant fragmentation of the olefinic pendent groups and linking groups from the polymeric backbone as a result of oxidation of the above compositions, article, layer and process.

In yet another preferred embodiment of the invention, the transition metal catalyst of the above oxygen scavenging composition, article of manufacture, layer and process is a metal salt.

In still another preferred embodiment of the invention, the metal in the metal salt of the above oxygen scavenging composition, article of manufacture, layer and process is cobalt.

In still another preferred embodiment of the invention, the metal salt of the above oxygen scavenging composition, article of manufacture, layer and process is selected from the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt oleate and cobalt stearate.

In yet another preferred embodiment of the invention, the composition of the above oxygen scavenging composition, article of manufacture, layer and process further comprises at least one triggering material to enhance initiation of oxygen scavenging.

In still another preferred embodiment of the invention, the triggering material of the above oxygen scavenging composition, article of manufacture, layer and process is a photo initiator.

In a preferred embodiment of the invention, the above article of manufacture is a package.

In another preferred embodiment of invention, the package article of the above article of manufacture comprises a flexible film having a thickness of at most 10 mil or a flexible sheet having a thickness of at least 10 mil.

In yet another preferred embodiment of the invention, the oxygen scavenging system of the package article of the above article of manufacture comprises at least one additional layer selected from among oxygen barrier layers, polymeric selective layers, and heat seal layers.

In still another preferred embodiment of the invention, the above article of manufacture is a package with a food product located within the package. In yet another preferred embodiment of the invention, the above article of manufacture is a package for packaging a cosmetic, chemical, electronic device, pesticide or a pharmaceutical composition.

In still another preferred embodiment of the invention, a multi-layer film comprises the article of the above article of manufacture and the film has at least one additional functional layer.

In yet another preferred embodiment of the invention, the multi-layer film of the above article of manufacture has at least one additional layer selected from among oxygen barrier layers, polymeric selective barrier layers, structural layers and heat seal layers.

In still another preferred embodiment of the invention, the multi-layer film of the above article of manufacture has at least one additional layer which is an oxygen barrier layer.

In yet another preferred embodiment of the invention, the multi-layer film of the above article of manufacture further comprises at least one polymeric selective barrier layer.

In still another preferred embodiment of the invention, the multi-layer film of the above article of manufacture further comprises at least one heat seal layer.

In yet another preferred embodiment of the invention, the multi-layer film of the above article of manufacture further comprises at least one structural layer.

In still another preferred embodiment of the invention, the above article of manufacture is a rigid container, sealing gasket, patch, container closure device, bottle cap, bottle cap insert or molded or thermoformed shape.

In yet another preferred embodiment of the invention, the molded or thermoformed shape of the above article of manufacture is a bottle or tray.

In still another preferred embodiment of the invention, the above layer in addition comprises polymeric diluent.

In yet another preferred embodiment of the invention, the diluent of the above layer is a thermoplastic polymer.

In still another preferred embodiment of the invention, the above layer is adjacent to one or more additional layers.

In still another preferred embodiment of the invention, at least one of the additional layers adjacent to the above layer is an oxygen barrier.

In still another preferred embodiment of the invention, the oxygen barrier of the above layer comprises a member of the group consisting of poly(ethylene-vinyl alcohol), polyacrylonitrile, poly(vinyl chloride), polyamides, poly(vinylidene dichloride), poly(ethylene terephthalate), silica, metal foil and metalized polymeric films.

In still another preferred embodiment of the invention, the one or more of said additional layer or layers of the above layer is coextruded with the above layer.

In yet another preferred embodiment of the invention, the one or more of said additional layer or layers of the above layer is laminated onto the above layer.

In still another preferred embodiment of the invention, the one or more of said additional layer or layers of the above layer is coated onto the above layer.

In yet another preferred embodiment of the invention, the above layer is flexible.

In still another preferred embodiment of the invention, the above layer is transparent.

In yet another preferred embodiment of the invention, an article for packaging wherein the article comprises the above layer.

In yet another preferred embodiment of the invention, the above process of making the oxygen scavenging packaging material comprises the steps of:

(a) selecting polymers from the group consisting of styrene/maleic anhydride, ethylene/maleic anhydride, ethylene/acrylic acid, ethylene/methacrylic acid, acrylic acid, methacrylic acid, styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate, and styrene/methyl methacrylate to form a mixture and combining the polymers with an esterifying/transesterifying compound selected from the group consisting of cyclohexene-4-methanol, 1-methyl cyclohexene-4-methanol, 2-methyl cyclohexene-4-methanol, 5-methyl cyclohexene-4-methanol, 1,2-dimethyl cyclohexene-4-methanol, 1,5-dimethyl cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,

1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol, 1-methyl cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol, 5-methyl cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol, 1,5-dimethyl cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-ethanol, 1,2,5-trimethyl cyclohexene-4-ethanol, cyclohexene-4-propanol, 1-methyl cyclohexene-4-propanol, 2-methyl cyclohexene-4-propanol, 5-methyl cyclohexene-4-propanol, 1,2-dimethyl cyclohexene-4-propanol, 1,5-dimethyl cyclohexene-4-propanol, 2,5-dimethyl cyclohexene-4-propanol, 1,2,5-trimethyl cyclohexene-4-propanol, cyclopentene-4-methanol, 1-methyl cyclopentene-4-methanol, 3-methyl cyclopentene-4-methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-dimethyl cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol, 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-4-ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-ethanol, 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl cyclopentene-4-ethanol, 1,3-dimethyl cyclopentene-4-ethanol, 2,3-dimethyl cyclopentene-4-ethanol, 1,2,3-trimethyl cyclopentene-4-ethanol, 1,2,3,5-tetramethyl cyclopentene-4-ethanol, cyclopentene-4-propanol, 1-methyl cyclopentene-4-propanol, 3-methyl cyclopentene-4-propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-dimethyl cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol, 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;

(b) heating the polymers and esterifying/transesterifying compounds selected in (a) to form a polymer melt;

(c) processing the melt in an extruder under esterification/transesterification conditions with esterification/transesterification catalysts and

antioxidants protecting the melt from oxidation during extrusion, so that the polymer melt undergoes esterification of polymeric anhydrides with cyclic olefin pendent groups, esterification of polymeric acids with cyclic olefin pendent groups or exchange of alkyl groups of polymeric esters with cyclic olefin pendent groups; and

(d) removing volatile organic products and by-products from the melt.

In still another preferred embodiment of the invention, the above process of making the oxygen scavenging packaging material comprises the steps of:

(a) selecting polymers from the group consisting of styrene/maleic anhydride, ethylene/maleic anhydride, ethylene/acrylic acid, ethylene/methacrylic acid, acrylic acid, methacrylic acid, styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate, and styrene/methyl methacrylate to form a mixture and combining the polymers with an amidizing/transamidizing compound selected from the group consisting of cyclohexene-4-methyl amine, 1-methyl cyclohexene-4-methyl amine, 2-methyl cyclohexene-4-methyl amine, 5-methyl cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-methyl amine, 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl cyclohexene-4-methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine, cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine, 2-methyl cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl amine, 1,2-dimethyl cyclohexene-4-ethyl amine, 1,5-dimethyl cyclohexene-4-ethyl amine, 2,5-dimethyl cyclohexene-4-ethyl amine, 1,2,5-trimethyl cyclohexene-4-ethyl amine, cyclohexene-4-propyl amine, 1-methyl cyclohexene-4-propyl amine, 2-methyl cyclohexene-4-propyl amine, 5-methyl cyclohexene-4-propyl amine, 1,2-dimethyl cyclohexene-4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl amine, 2,5-dimethyl

cyclohexene-4-propyl amine, 1,2,5-trimethyl cyclohexene-4-propyl amine, cyclopentene-4-methyl amine, 1-methyl cyclopentene-4-methyl amine, 3-methyl cyclopentene-4-methyl amine, 1,2-dimethyl cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl amine, 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-4-ethyl amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl cyclopentene-4-ethyl amine, 1,2-dimethyl cyclopentene-4-ethyl amine, 3,5-dimethyl cyclopentene-4-ethyl amine, 1,3-dimethyl cyclopentene-4-ethyl amine, 2,3-dimethyl cyclopentene-4-ethyl amine, 1,2,3-trimethyl cyclopentene-4-ethyl amine, 1,2,3,5-tetramethyl cyclopentene-4-ethyl amine, cyclopentene-4-propyl amine, 1-methyl cyclopentene-4-propyl amine, 3-methyl cyclopentene-4-propyl amine, 1,2-dimethyl cyclopentene-4-propyl amine, 3,5-dimethyl cyclopentene-4-propyl amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-dimethyl cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;

(b) heating the polymers and amidizing/transamidizing compounds selected in (a) to form a polymer melt;

(c) processing the melt in an extruder under amidation/transamidation conditions with amidation/transamidation catalysts and antioxidants protecting the melt from oxidation during extrusion, so that the polymer melt undergoes amidation of polymeric anhydrides with cyclic olefin pendent groups, amidation of polymeric acids with cyclic olefin pendent groups or exchange of alkyl groups of polymeric esters with cyclic olefin pendent groups; and

(d) removing volatile organic products and by-products from the melt.

In yet another preferred embodiment of the invention, the above process of making of the oxygen scavenging packaging material comprises the steps of:

(a) adding to an autoclave, ethylene and a vinyl monomer comprising a pendent cyclohexene;

(b) stirring the ethylene and the vinyl monomer in the autoclave to achieve a mixture;

(c) adding a polymerization initiator before, during or after the stirring step;

(d) polymerizing the mixture to achieve a polymer; and

(e) isolating and purifying the polymer.

In still another embodiment of the invention, in the above process, in step (a), an alpha-olefin is added to the autoclave along with the ethylene and the vinyl monomer and, in step (b), the alpha-olefin is stirred with the ethylene and the vinyl monomer to achieve the mixture.

The present invention relates to a non-odorous oxygen scavenging polymer composition comprising: (1) monomers derived from cyclic hydrocarbon moieties having at least one cyclic allylic or cyclic benzylic hydrogen and (2) a transition metal oxidation catalyst. The present invention also relates to a rigid container for food or beverage, the container being molded from a resin comprising the above-described non-odorous oxygen scavenging polymer composition. The present invention also relates to the above-described rigid container further comprising a tinted ultraviolet protection layer, which may or may not be the food contact layer, located between the layer comprising the non-odorous oxygen scavenging composition and the inside of the rigid container.

In a preferred embodiment of the above non-odorous oxygen scavenging polymer composition, wherein the composition comprises a vinyl polymer selected from the group consisting of ethylene polymer, ethylene copolymer, propylene polymer, propylene copolymer, styrene polymer, styrene copolymer and mixtures thereof.

In another preferred embodiment of the above non-odorous oxygen scavenging polymer composition, the composition comprises condensation polymers selected from the group consisting of polyesters, polyamides, polycarbonate, polyurethane, polyureas and polyether.

In a more preferred embodiment of the above composition comprising condensation polymers, the composition is thermoplastic.

In another more preferred embodiment of the above composition comprising condensation polymers, the composition is thermoset.

In yet another more preferred embodiment of the above composition comprising condensation polymers, the composition is a multilayered structure with other layers being an aromatic polyester or copolyester selected from the group consisting of polyethylene terephthalate, polyethylene naphthalate, polypropylene terephthalate, polybutylene terephthalate, polyethylene isophthalate, polycyclohexanedimethanol terephthalate, polybutylene naphthalate, polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

In still another more preferred embodiment of the above composition comprising condensation polymers, the composition is a multilayered structure with other layers being polyamides or copolyamides selected from the group consisting of Nylon 6, Nylon 66, Nylon 610 and mixtures thereof.

In yet another more preferred embodiment of the above composition comprising condensation polymers, the composition is a multilayered structure with other layers being bisphenol A carbonate.

In yet another more preferred embodiment of the above composition comprising condensation polymers, the composition is a multilayered structure with other layers being vinylic polymers or copolymers selected from the group consisting of ethylene polymer, ethylene copolymer, propylene polymer, propylene copolymer, styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer, vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer, divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl copolymer and mixtures thereof.

In still another more preferred embodiment of the above composition comprising condensation polymers, the composition is blended with an aromatic polyester or copolyester selected from the group consisting of polyethylene terephthalate, polyethylene naphthalate, polypropylene terephthalate, polybutylene terephthalate, polyethylene isophthalate, polycyclohexandedimethanol terephthalate, polybutylene naphthalate, polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

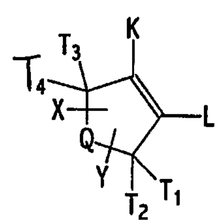
In yet another more preferred embodiment of the above composition comprising condensation polymers, the composition is blended with polyamides or copolyamides selected from the group consisting of Nylon 6, Nylon 66, Nylon 610 and mixtures thereof.

In still another more preferred embodiment of the above composition comprising condensation polymers, the composition is blended with bisphenol A polycarbonate.

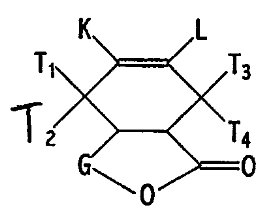
In yet another more preferred embodiment of the above composition comprising condensation polymers, the composition being a blend comprising vinylic polymers or copolymers selected from the group consisting of ethylene polymer, ethylene copolymer, propylene polymer, propylene copolymer, styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer, vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer, divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl copolymer and mixtures thereof.

In a more preferred embodiment of the above composition comprising condensation polymers, the composition is laminated or adhering onto a substrate selected from the group consisting of paper, foil, high temperature film, metallized film, polyamide films, ethylene vinyl alcohol film, silica coated film, nylon/EVOH/nylon, oriented polypropylene, polyester film, polyethylene, polypropylene, polyester, oriented polyethylene terephthalate and cellophane.

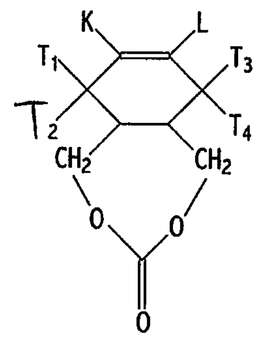
In another preferred embodiment of the above non-odorous oxygen scavenging polymer composition, the cyclic allylic monomers are selected from the group consisting of structure (V), structure (VI) and structure (VII):



(V)



(VI)

(VII) 

with K, L, T_1, T_2, T_3, and T_4 being selected from the group consisting of

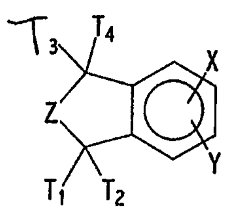
$-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and wherein, when either K or L is –H, at least one of T_1, T_2, T_3 and T_4 is –H;

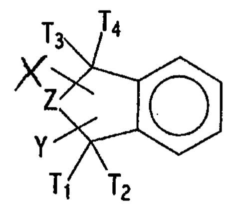
and with X and Y being selected from the group consisting of $-(CH_2)_n$-OH, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC=O$ and $-(CH_2)_m-(C=O)-A$ with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of –OH, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides; and Q being selected from the group consisting of $-(C_tH_{2t-2})$ with t being an integer in the range from 1 to 4;

and with G being selected from –(C=O)- and $-(C_nH_{2n+1})-$ with n being an integer from 0 to 12.

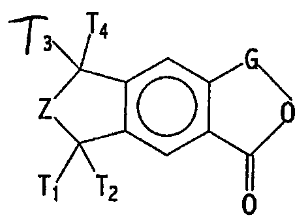
In yet another more preferred embodiment of the above non-odorous oxygen scavenging polymer composition, the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII)

(VIII)

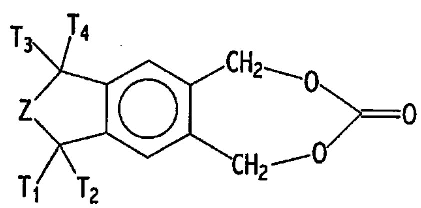




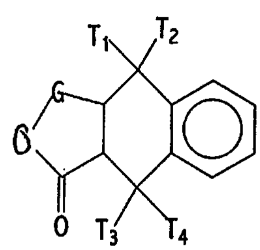
(IX)



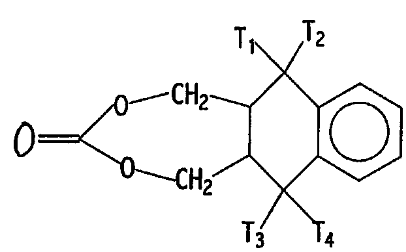
(X)



(XI)



(XII)



(XIII)

where X and Y are selected from the group consisting of $-(CH_2)_n-OH$, $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C{=}O)-R_1$ with n being an integer in the range

from 1 to 12, and with m being an integer in the range from 0 to 12 and with R_1 being selected from the group consisting of –OH, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;

with T_1, T_2, T_3, and T_4 being selected from the group consisting of $-C_qH_{2q+1}$ with q being an integer in the range from 0 to 12 and at least one of T_1, T_2, T_3 and T_4 being –H;

and with X and Y being selected from the group consisting of –$(CH_2)_n$-OH, $-(CH_2)_n-NH_2$, $-(CH_2)_nNC{=}O$, and $-(CH_2)_m-(C{=}O)-A$ with n being an integer in the range from 1 to 12, and m being an integer in the range from 0 to 12 and A being selected from the group consisting of -OH, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides; and Z being selected from the group consisting of $-(C_tH_{2t-2})-$, -O-, $-NR_2-$, -S-, with t being an integer in the range from 1 to 4 and R_2 being selected from the group consisting of –OH, $-OCH_3$, $-OC_2H_5$, $-OC_3H_7$ and halides;

and with G being selected from –(C=O)- and $-(C_nH_{2n+1})-$ with n being an integer from 0 to 12.

In still another more preferred embodiment, the composition of the resin of the above-described rigid container is a single layer.

In yet another more preferred embodiment, the composition of the resin of the above-described rigid container is multilayered.

In yet another more preferred embodiment, the composition of the resin of the above-described rigid container comprises an outer air contact layer and an inner oxygen scavenging layer.

In still another more preferred embodiment, the outer air contact layer of the composition of the resin of the above-described rigid container comprises an oxygen barrier resin selected from the group consisting of polyethylene

terephthalate, polyethylene naphthalate and a mixture of polyethylene terephthalate and polyethylene naphthalate.

In yet another more preferred embodiment, the composition of the resin of the above-described rigid container further comprises at least one of an inner food contact layer, a tie layer, and a tinted ultraviolet protection layer.

In still another more preferred embodiment, the inner food contact layer of the composition of the resin of the above-described rigid container comprises an oxygen barrier resin selected from the group consisting of polyethylene terephthalate, polyethylene naphthalate and a mixture of polyethylene terephthalate and polyethylene naphthalate.

In yet another more preferred embodiment, the oxygen scavenging of the composition of the resin of the above-described rigid container is initiated by moisture or actinic radiation.

In still another more preferred embodiment, the transition metal catalyst of the composition of the resin of the above-described rigid container is a metal salt.

In yet another more preferred embodiment, the metal in the metal salt of the transition metal catalyst of the composition of the resin of the above-described rigid container is cobalt.

In still another more preferred embodiment, the metal salt of the transition metal catalyst of the composition of the resin of the above-described rigid container is selected from the group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt oleate and cobalt stearate.

In yet another more preferred embodiment, the composition of the resin of the above-described rigid container further comprises at least one triggering material to enhance initiation of oxygen scavenging.

In still another more preferred embodiment, the triggering material of the resin of the composition of the above-described rigid container is a photoinitiator.

In yet another more preferred embodiment, the photoinitiator of the resin of the composition of the above-described rigid container has an ultraviolet absorption window above 320 nm.

In still another more preferred embodiment, the above-described rigid container is suitable for packaging oxygen sensitive drinks for extended freshness and shelf life.

In yet another more preferred embodiment, the above-described rigid container is suitable for packaging beer.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic showing the overall process leading to the transesterification of ethylene methyl acrylate copolymers (EMAC) to give modified EMAC having cyclic pendent olefins.

Figure 2 is a graph comparatively plotting percent oxygen in headspace at 4°C (initially at 1% oxygen) against time in days for two 3-layer film extrusions based on Dowlex® 3010/EMCM/Dowlex® 3010 films (EMCM being an acronym for ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer also referred to as poly(ethylene/methyl acrylate/cyclohexene-methyl acrylate)), both including the EMCM inner layer and one of them having

50 ppm of a non-volatile antioxidant Irganox® 1010 in the EMCM layer and one of them having 100 ppm Irganox® 1010 in the EMCM layer.

Figure 3 is a graph comparatively plotting percent oxygen in headspace at 4°C (initially at 1% oxygen) against time in days for an EMCM film and two EBAC blended EMCM films, one of them having 3:1 EBAC:EMCM and one of them having 1:1 EBAC:EMCM.

Figure 4 is a graph comparatively plotting the oxygen scavenging rates and capacities at 25°C in which the initial headspace oxygen was 21% (air) for an EMCM film and a 2:1 EBAC:EMCM film.

Figure 5 is a graph showing the taste ratings in a comparative taste test between food stored in two oxygen scavenging packages (EMCM and SBS) and a control package (no oxygen scavenger).

DETAILED DESCRIPTION OF THE INVENTION

We have found that materials containing certain cyclohexenyl functionalities are excellent oxygen absorbers when compounded with a transition metal salt and optionally a photoinitiator, and that when these materials oxidize they produce very low levels of oxidation byproducts. This is in marked contrast to the known art, where excellent oxygen absorbers can be obtained from the use of linear unsaturated compounds compound with a transition metal slat, and a photoinitiator, but where the levels of oxidation byproducts are excessively high. It is thought that this improvement is obtained because mild oxidation of cyclohexene does not break bonds on the ring structure whilst oxidation of linear unsaturated material such as linoleic acid or vegetable oil

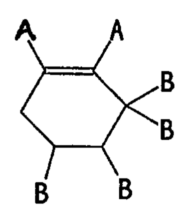
under similar conditions produces smaller molecules by chain scission. When incorporated into polymers, the cyclohexene containing systems are found to produce considerably less volatile byproducts than the linear unsaturated materials.

The compositions of this invention are significantly cleaner than those described in the prior art, they do not require the use of high levels of adjuncts to absorb the undesirable byproducts. Such absorbent additives are known in the art, for example see U.S. 5,834,079 and U.S. 08/857,276. It is also well known in the art that such additives (zeolites and silicas) adversely affect the haze and clarity of packaging structures.

The oxygen scavenging compositions consist of:

(a) a polymer or lower molecular weight material containing substituted cyclohexene functionality according to the following structure (I):

(I)



where A may be hydrogen or methyl and either one or two of the B groups is a heteroatom containing linkage which attaches the cyclohexene ring to the said material. The remaining B groups are hydrogen or methyl;

(b) a transition metal catalyst;

(c) an optional photoinitiator.

The compositions may be polymeric in nature or they may be lower molecular weight materials. In either case, they may be blended with further polymers or other additives. In the case of low molecular weight materials they will most likely be compounded with a carrier resin before use. The following examples represent some applications of various embodiments of the present invention currently envisaged by the patentee. These examples are not meant to be limiting nor exhaustive but merely illustrative of how the present invention may be used, or applied to address problems associated with the prior art.

The compositions of this invention can be used in a wide range of packaging materials, and are not restricted to flexible packaging films and articles such as pouches produced from such films. The compositions may also be used in the preparation of rigid and semi rigid packaging materials. Typical rigid and semi rigid articles include plastic, paper or cardboard cartons, bottles such as juice containers, thermoformed trays, or cups with wall thicknesses of about 100 to 2000 microns. The walls of such articles comprise single or multiple layers of materials. The compositions can be used as the sole polymeric material from which one or more layers of a film are formed (i.e., the film can be a multilayer film having, for example, a gas barrier layer, a seal layer, etc.), it can be blended with other polymeric oxygen scavenging agents (such as polybutadiene) or it can be blended with one or more diluent polymers which are known to be useful in the formation of packaging film materials and which often can render the resultant film more flexible and/or processable. Suitable diluent polymers include, but are not limited to, polyethylene such as, for example, low density polyethylene, very low density polyethylene, ultra-low

density polyethylene, high density polyethylene, and linear low density polyethylene; polyesters such as, for example, polyethylene terephthalate (PET); polyvinyl chloride (PVC); polyvinylidene chloride (PVDC); and ethylene copolymers such as ethylene/vinyl acetate copolymer, ethylene/alkyl (meth)acrylate copolymers, ethylene/(meth)acrylic acid copolymers, and ionomers. Blends of different diluent polymers also can be used.

The compositions of this invention can also be used in non integral packaging components such as coatings, bottle cap liners, adhesive and non adhesive sheet inserts, coupons, gaskets, sealants or fibrous mass inserts.

Generally, the foregoing diluent polymers are semi-crystalline materials. Advantageously, the polymeric component of the composition of the present invention can be crystalline or semi-crystalline at ambient conditions and, accordingly, can be especially compatible with such diluent polymers. Selection of a particular diluent polymer(s) depends largely on the article to be manufactured and the end use thereof. For instance, certain polymers are known by the ordinarily skilled artisan to provide clarity, cleanliness, barrier properties, mechanical properties, and/or texture to the resultant article.

In combination with the polymeric component, the oxygen scavenging composition of the present invention includes a transition metal compound as an oxygen scavenger catalyst. The transition metal catalyst can be a slat which includes a metal selected from the first, second, or third transition series of the Periodic Table. The metal preferably is Rh, Ru, or one of the elements in the series of Sc to Zn (i.e., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn), more preferably at least one of Mn, Fe, Co, Ni, and Cu, and most preferably Co. Suitable anions for such salts include, but are not limited to, chloride, acetate, oleate, stearate, palmitate, 2-ethylhexanoate, neodecanoate, and naphthenate. Representative salts include cobalt (II)

2-ethylhexanoate, cobalt oleate, and cobalt (II) neodecanoate. (The metal salt also can be an ionomer, in which case a polymeric counterion is employed.)

When used in forming a packaging article, the oxygen scavenging composition of the present invention can include only the above-described polymers and a transition metal catalyst. However, photoinitiators can be added to further facilitate and control the initiation of oxygen scavenging properties. Adding a photoinitiator or a blend of photoinitiators to the oxygen scavenging composition can be preferred, especially where antioxidants have been added to prevent premature oxidation of the composition during processing and storage.

Suitable photoinitiators are known to those skilled in the art. See, e.g., PCT Publication WO 97/07161, WO 97/44364, WO 98/51758, and WO 98/51759, the teachings of which are incorporated herein by reference as if set forth in full. Specific examples of suitable photoinitiators include, but are not limited to, benzophenone, and its derivatives, such as methoxybenzophenone, dimethoxybenzophenone, dimethylbenzophenone, diphenoxybenzophenone, allyloxybenzophenone, diallyloxybenzophenone, dodecyloxybenzophenone, dibenzosuberone, 4,4'-bis(4-isopropylphenoxy)benzophenone, 4-morpholinobenzophenone, 4-aminobenzophenone, tribenzoyl triphenylbenzene, tritoluoyl triphenylbenzene, 4,4'-bis(dimethylamino)-benzophenone, acetophenone and its derivatives, such as, o-methoxy-acetophenone, 4'-methoxyacetophenone, valerophenone, hexanophenone, α-phenyl-butyrophenone, p-morpholinopropiophenone, benzoin and its derivatives, such as, benzoin methyl ether, benzoin butyl ether, benzoin tetrahydropyranyl ether, 4-o-morpholinodeoxybenzoin, substituted and unsubstituted anthraquinones, α-tetralone, acenaphthenequinone, 9-acetylphenanthrene, 2-acetyl-phenanthrene, 10-thioxanthenone, 3-acetyl-

phenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, isopropylthioxanthen-9-one, xanthene-9-one, 7-H-benz[de]anthracen-7-one, 1'-acetonaphthone, 2'-acetonaphthone, acetonaphthone, benz[de]anthracen-7-one, 1'-acetonaphthone, 2'-acetonaphthone, acetonaphthone, benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone, α,α-diethoxyacetophenone, α,α-dibutoxyacetophenone, 4-benzoyl-4'-methyl(diphenyl sulfide) and the like. Single oxygen-generating photosensitizers such as Rose Bengal, methylene blue, and tetraphenylporphine as well as polymeric initiators such as poly(ethylene carbon monoxide) and oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone] also can be used. However, photoinitiators are preferred because they generally provide faster and more efficient initiation. When actinic radiation is used, photoinitiators can provide initiation at longer wavelengths which are less costly to generate and present less harmful side effects than shorter wavelengths.

When a photoinitiator is present, it can enhance and/or facilitate the initiation of oxygen scavenging by the composition of the present invention upon exposure to radiation. The amount of photoinitiator can depend on the amount and type of cyclic unsaturation present in the polymer, the wavelength and intensity of radiation used, the nature and amount of antioxidants used, and the type of photoinitiator used. The amount of photoinitiator also can depend on how the scavenging composition is used. For instance, if a photoinitiator-containing composition is in a film layer, which underneath another layer is somewhat opaque to the radiation used, more initiator might be needed. However, the amount of photoinitiator used for most applications ranges from about 0.01 to about 10% (By wt.) of the total composition. Oxygen scavenging can be initiated by exposing an article

containing the composition of the present invention to actinic or electron beam radiation, as described below.

One or more antioxidants can be incorporated into the scavenging composition of the present invention to retard degradation of the components during compounding and film formation. Although such additives prolong the induction period for oxygen scavenging activity to occur in the absence of irradiation, the layer or article (and any incorporated photoinitiator) can be exposed to radiation at the time oxygen scavenging properties are required. Suitable antioxidants include 2,6-di(t-butyl)-4-methylphenol(BHT), 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite, tris-(nonylphenyl)phosphite, dilaurylthiodipropionate, vitamin E (α-tocopherol), octadecyl 3,5,-di-tert-butyl-4-hydroxyhydrocinnamate, tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane and the like.

When an antioxidant is included as part of the composition of the present invention, it preferably is present in an amount which prevents oxidation of the components of the oxygen scavenging composition as well as other materials present in a resultant blend during formation and processing; however, the amount preferably is less than that which interferes with the scavenging activity of the resultant layer, film, or article after initiation has occurred. The amount needed in a given composition can depend on the components present therein, the particular antioxidant used, the degree and amount of thermal processing used to form the shaped article, and the dosage and wavelength of radiation applied to initiate oxygen scavenging. Typically, such antioxidant(s) are used in an amount of from about 0.01 to about 1% (by wt.).

Other additives that also can be included in the oxygen scavenging composition of the present invention include, but are not necessarily limited

to, fillers, pigments, dyestuffs, processing aids, plasticizers, antifog agents, antiblocking agents, and the like.

The amounts of the components used in the oxygen scavenging composition of the present invention can affect the use and effectiveness of this composition. Thus, the amounts of polymer, transition metal catalyst, and any photoinitiator, antioxidant, polymeric diluents, additives, etc., can vary depending on the desired article and its end use. For example, one of the primary functions of the polymer described above is to react irreversibly with oxygen during the scavenging process, while a primary function of the transition metal catalyst is to facilitate this process. Thus, to a large extent, the amount of polymer present affects the oxygen scavenging capacity of the composition, i.e., the amount of oxygen that the composition can consume, while the amount of transition metal catalyst affects the rate at which oxygen is consumed as well as the induction period.

The composition of the present invention can provide oxygen scavenging properties at a desirable rate and capacity while having good processing and compatibility properties relative to compositions including conventional non-cyclic ethylenically unsaturated polymers. Thus, the present composition can be used to provide, by itself or as a blend with diluent film-forming polymers such as polyolefins and the like, a packaging material or film that can be manufactured and processed easily. Further, the subject oxygen scavenging composition will deplete the oxygen within a package cavity without substantially detracting from the color, taste, and/or odor of the product contained therein.

The amount of the polymeric scavenging component contained in the subject composition can range from about 1 to almost about 100%, preferably from about 5 to about 97.5%, more preferably from about 10 to 95%, even more

preferably from about 15 to about 92.5%, still more preferably from about 20 to about 90%, (with all the foregoing percentages being by weight) of the composition or layer made therefrom. Typically, the amount of transition metal catalyst can range from 0.001 to 1% (by wt.) of the scavenging composition, based on the metal content only (i.e., excluding ligands, counterions, etc.). Where one or more other scavenging compounds and/or diluent polymers are used as part of the composition, such other materials can make up as much as 99%, preferably up to about 75%, by weight of the scavenging composition. Any further additives employed normally do not make up more than 10%, preferably no more than about 5%, by weight of the scavenging composition.

As indicated above, the composition of the present invention can be used to produce a scavenging monolayer film, a scavenging layer of a multilayer film, or other articles for a variety of packaging applications. Single layer articles can be prepared readily by extrusion processing. Multilayer films typically are prepared using coextrusion, coating, lamination or processing. Multilayer films typically are prepared using coextrusion, coating, lamination or extrusion/lamination as taught in, for example, U.S. Patents 5,350,622 and 5,529,833, the teachings of which are incorporated herein by reference as if set forth in full. At least one of the additional layers of multilayer article can include a material having a permeance to oxygen of no more than about 5.8×10^{-8} $cm^3/m^2 \bullet s \bullet Pa$ (i.e., about 500 $cm^3/m^2 \bullet 24$ hours$\bullet$atm) at about 25°C. Polymers which are commonly used in such oxygen barrier layers include poly(ethylene/vinyl alcohol), poly(vinyl alcohol), polyacrylonitrile, PVC, PVDC, PET, silica, and polyamides such as nylon 6, MXD6, nylon 66, as well as various amide copolymers. (Metal foil layers can also provide oxygen barrier properties.) Other additional layers can include on or more layers which are permeable to oxygen. In one preferred packaging construction, especially flexible packages for food, the layers can include (in order starting from the

outside of the package to the innermost layer of the package) (a) an oxygen barrier layer, (b) a scavenging layer, i.e. one that includes the scavenging composition described supra, and optionally, (c) an oxygen permeable layer. Control of the oxygen barrier property of layer (a) provides a means to regulate the scavenging life of the package by limiting the rate of oxygen entry to the scavenging layer (b), thus limiting the rate of consumption of scavenging capacity. Control of the oxygen permeability of layer (c) provides a means to set an upper limit on the rate of oxygen scavenging for the overall structure independent of the composition of scavenging layer (b). This can serve the purpose of extending the handling lifetime of the film in the presence of air prior to sealing of the package. Furthermore, layer (c) can provide a barrier to migration of the individual components or byproducts of the scavenging layer into the package interior. The term "exposed to the interior" refers to a portion of a packaging article having the subject scavenging composition which is either directly exposed or indirectly exposed (via layers which are O_2 permeable) to the interior cavity having oxygen sensitive product. Even further, layer (c) also can improve the heat sealability, clarity, and/or resistance to blocking of the multilayer film. Further additional layers such as the layers, easy open layers, and seal layers can also be used. Polymers typically used in such tie layers include, for example, anhydride functional polyolefins.

The method of the present invention includes exposing the above-described composition to a package cavity having an oxygen sensitive product therein. A preferred embodiment provides for including a photoinitiator as part of the subject composition and subjecting a film, layer, or article that includes such a composition to radiation so as to initiate oxygen scavenging at desired rates. The thermal radiation used in heating and processing polymers typically used in packaging films (e.g., 100-250°C) advantageously does not trigger the oxygen scavenging reaction.

The initiating radiation preferably is actinic, e.g., UV or visible light having a wavelength of from about 200 to about 750 nm, preferably of from about 200 to 600 nm, and most preferably from about 200 to 400 nm. Such light can be delivered in a continuous or pulsed manner. The layer, film, etc., containing the oxygen scavenging composition preferably is exposed to such radiation until it receives at least about 1 J/g of radiation, more preferably until it receives a dose in the range of about 10 to about 2000 J/g. The radiation also can be electron-beam radiation at a dosage of at least about 2 kiloGray (kG), preferably from about 10 to about 100 kG. Other potential sources of radiation include ionizing radiation such as gamma, X-ray, and corona discharge. Duration of exposure depends on several factors including, but not limited to, the amount and type of photoinitiator present, thickness of the layers to be exposed, thickness and opacity of intervening layers, amount of any antioxidant present, and the wavelength and intensity of the radiation source.

When using oxygen scavenging layers or articles, irradiation can occur during or after the layer or article is prepared. If the resulting layer or articles is to be used to package an oxygen sensitive product, exposure can be just prior to, during, or after packaging. For best uniformity of radiation, exposure preferably occurs at a processing stage where the layer or article is in the form of a flat sheet. For further information on initiation via irradiation, the reader is directed to PCT publications WO 98/05555 and WO 98/05703, as well as PCT 97/13598, 97/13370, 97/13369, the teachings of which are incorporated herein by reference.

Determining the oxygen scavenging rate and capacity of a given oxygen scavenging composition contemplated for a particular use can be beneficial. To determine the rate, the time elapsed before the scavenger depletes a

certain amount of oxygen from a sealed container is measured. In some instances, the rate can be determined adequately by placing a film containing the desired scavenging composition in an air-tight, sealed container of an oxygen containing atmosphere, e.g., air which typically contains 20.6% (by vol.) O_2. Over time, samples of the atmosphere inside the container are removed to determine the percentage of oxygen remaining. (Usually, the specific rates obtained vary under different temperature and atmospheric conditions. Atmospheres having lower initial oxygen content and/or maintained under low temperature conditions provide a more stringent test of the scavenging ability and rate of a composition. The rates which follow are at room temperature and one atmosphere of air, unless otherwise specified.) When an active oxygen barrier is needed, a useful scavenging rate can be as low as about 0.05 cm^3 oxygen per gram of the polymer in the scavenging composition per day in air at 25°C and at 1 atm (101.3 kPa). However, in most instances, the present composition has a rate equal to or greater than about 5.8×10^{-8} $cm^3/g \bullet s$(0.5 $cm^3/g \bullet day$), even up to or greater than about 5.8×10^{-5} $cm^3/g \bullet s$ (5 $cm^3/g \bullet day$). Further, films or layers including the subject composition are capable of a scavenging rate greater than about 1.2×10^{-4} $cm^3/m^2 \bullet s$ (10 $cm^3/m^2 \bullet day$) and under some conditions, greater than about 2.9×10^{-4} $cm^3/m^2 \bullet s$ (25 $cm^3/m^2 \bullet day$). (Generally, films or layers generally deemed suitable for use as an active oxygen barrier can have a scavenging rate as low as 1.2×10^{-5} $cm^3/m^2 \bullet s$ (1 $cm^3/m^2 \bullet day$) when measured in air at 25°C and 101 kPa (1 atm). Such rates make those layers suitable for scavenging oxygen from within a package, as well as suitable for active oxygen barrier applications.

When the method of the present invention is to be used in an active oxygen barrier application, the initiated oxygen scavenging activity, in combination with any oxygen barriers, preferably creates an overall oxygen permeance of less than about 1.1×10^{-10} $cm^3/m^2 \bullet s \bullet Pa$ (1.0 $cm^3/m^2 \bullet day \bullet atm$) at 25°C. The

oxygen scavenging capacity preferably is such that this value is not exceeded for at least two days.

Once scavenging has been initiated, the scavenging composition, layer, or article prepared therefrom preferably is able to scavenge up to its capacity, i.e., the amount of oxygen which the scavenger is capable of consuming before it becomes ineffective. In actual use, the capacity required for a given application can depend on the quantity of oxygen initially present in the package, the rate of oxygen entry into the package in the absence of the scavenging property, and the intended shelf life for the package. When using scavengers that include the composition of the present invention, the capacity can be as low as 1 cm^3/g, but can be 50 cm^3/g or higher. When such scavengers are in a layer of a film, the layer preferably has an oxygen capacity of at least about 9.8 cm^3/m^2 per μm thickness (1200 cm^3/m^2 per mil).

The composition of the present invention has been found to be capable of providing a film, layer or article which substantially retains its physical properties (e.g., tensile strength and modulus) even after substantial oxygen scavenging has occurred. In addition, the present composition does not provide significant amounts of byproducts and/or effluents, which can impart an undesired taste, color, and/or odor to the packaged product.

This invention relates to an oxygen scavenging polymer composition comprising cyclic allylic pendent groups which can be used in oxygen scavenging packaging material which have either no or low volatile oxidation by-products. Minimizing volatile by-products reduces the problem of organoleptics in oxygen scavenging food packaging.

The polymer composition with cyclic allylic pendent groups can be made by grafting methyl cyclohex-1-ene-4-methanol, cyclohex-1-ene-4-methanol

(1,2,5,6-tetrahydrobenzyl alcohol) and cyclohex-1-ene-4-propanol onto EMAC resins by transesterification of the corresponding alcohols or transamidation of the corresponding amines with the methyl esters on EMAC to give modified EMAC having pendent cyclic olefins (see Figure 1). The composition can also be made by direct polymerization.

The esterification, transesterification, amidation or transamidation reaction can be a solution reaction or by reactive extrusion. The catalysts can be any one of strong non-oxidizing acids, tertiary amines, Group I alkoxides, Group IVB alkoxides and Group IVA metal organics. The level of olefin in the final products can be controlled by the level of transesterification and the methyl ester content of the start EMAC. The molecular weight of the polymers largely depends on the molecular weight of the EMAC feeds.

In a preferred embodiment, these products are combined with a transition-metal salt to catalyze the oxygen scavenging properties of the materials. A transition-metal salt, as the term is used here, comprises an element chosen from the first, second and third transition series of the periodic table of the elements, particularly one that is capable of promoting oxidation reactions. This transition-metal salt is in a form which facilitates or imparts scavenging of oxygen by the composition of this invention. A plausible mechanism, not intended to place limitations on this invention, is that the transition element can readily inter-convert between at least two oxidation states and facilitates formation of free radicals. Suitable transition-metal elements include, but are not limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III, copper I or II, rhodium II, III or IV, and ruthenium. The oxidation state of the transition-metal element when introduced into the composition is not necessarily that of the active form. It is only necessary to have the transition-metal element in its active form at or shortly before the time that the composition is required to scavenge oxygen. The transition-metal element is

preferably iron, nickel or copper, more preferably manganese and most preferably cobalt.

Suitable counter-ions for the transition metal element are organic or inorganic anions. These include, but are not limited to, chloride, acetate, stearate, oleate, palmitate, 2-ethylhexanoate, citrate, glycolate, benzoate, neodecanoate or naphthenate. Organic anions are preferred. Particularly preferable salts include cobalt 2-ethylhexanoate, cobalt benzoate, cobalt stearate, cobalt oleate and cobalt neodecanoate. The transition-metal element may also be introduced as an ionomer, in which case a polymeric counter-ion is employed.

The composition of the present invention when used in forming a oxygen scavenging packaging article can be composed solely of the above described polymer and transition metal catalyst. However, components, such as photoinitiators, can be added to further facilitate and control the initiation of oxygen scavenging properties. For instance, it is often preferable to add a photoinitiator, or a blend of different photoinitiators, to the oxygen scavenger compositions, especially when antioxidants are included to prevent premature oxidation of that composition during processing.

Suitable photoinitiators are well known in the art. Such photoinitiators are discussed in U.S. Patent No. 5,211,875. It is also discussed in U.S. Patent Application Serial No. 08/857,325, in which some of the present inventors were contributing inventors and which is incorporated herein by reference. Specific examples include, but are not limited to, benzophenone, o-methoxy-benzophenone, acetophenone, o-methoxy-acetophenone, acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone, α-phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, benzoin, benzoin methyl ether, 4-o-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone,

4'-methoxyacetophenone, substituted and unsubstituted anthraquinones, α-tetralone, 9-acetylphenanthrene, 2-acetyl-phenanthrene, 10-thioxanthenone, 3-acetyl-phenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one, 7-H-benz[de]anthracen-7-one, benzoin tetrahydropyranyl ether, 4,4'-bis(dimethylamino)-benzophenone, 1'-acetonaphthone, 2'-acetonaphthone, acetonaphthone and 2,3-butanedione, benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone, α,α-diethoxy-acetophenone, α,α-dibutoxyacetophenone, etc. Singlet oxygen generating photosensitizers such as Rose Bengal, methylene blue, and tetraphenyl porphine may also be employed as photoinitiators. Polymeric initiators include polyethylene carbon monoxide and oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone]. Use of a photoinitiator is preferable because it generally provides faster and more efficient initiation.

When a photoinitiator is used, its primary function is to enhance and facilitate the initiation of oxygen scavenging upon exposure to radiation. The amount of photoinitiator can vary. In many instances, the amount will depend on the amount and type of oxygen scavenging polymer in the present invention, the wavelength and intensity of radiation used, the nature and amount of antioxidants used, as well as the type of photoinitiator used. The amount of photoinitiator also depends on how the scavenging composition is used. For instance, if the photoinitiator-coating composition is placed underneath a layer which is somewhat opaque to the radiation used, more initiator may be needed. For most purposes, however, the amount of photoinitiator, when used, will be in the range of 0.01 to 10% by weight of the total composition. The initiating of oxygen scavenging can be accomplished by exposing the packaging article to actinic or electron beam radiation, as described below.

Antioxidants may be incorporated into the scavenging compositions of this invention to control degradation of the components during compounding and shaping. An antioxidant, as defined herein, is any material which inhibits oxidative degradation or cross-linking of polymers. Typically, such antioxidants are added to facilitate the processing of polymeric materials and/or prolong their useful shelf-life.

Antioxidants such as Vitamin E, Irganox® 1010, Irganox® 1076, 2,6-di(t-butyl)-4-methyl-phenol(BHT), 2,6-di(t-butyl)-4-ethyl-phenol (BHEB), 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite, tris-(nonylphenyl)phosphite and dilaurylthiodipropionate would be suitable for use with this invention.

When an antioxidant is included as part of the present composition, it should be used in amounts which will prevent oxidation of the scavenger composition's components as well as other materials present in a resultant blend during formation and processing but the amount should be less than that which would interfere with the scavenging activity of the resultant layer, film or article. The particular amount needed will depend on the particular components of the composition, the particular antioxidant used, the degree and amount of thermal processing used to form the shaped article, and the dosage and wavelength of radiation applied to initiate oxygen scavenging and can be determined by conventional means. Typically, they are present in about 0.01 to 1% by weight.

Other additives which may also be included in oxygen scavenger layers include, but are not necessarily limited to, fillers, pigments, dyestuffs, stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, etc.

The amounts of the components which are used in the oxygen scavenging compositions, or layers have an effect on the use, effectiveness and results of